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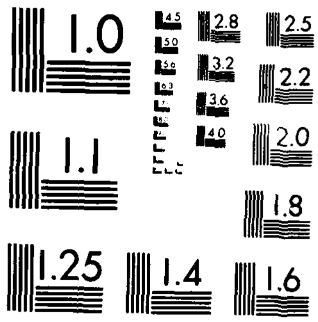

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ENGINE WEAR WITH METHANOL FUEL IN A NITROGEN-FREE ENVIRONMENT

INTERIM REPORT
AFLRL No. 175

By

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Several test programs have shown that the combustion of methanol in spark ignition engines can cause unusually high corrosive wear of the upper cylinder bore and ring areas. In this study, a 2.3-liter engine fueled with methanol was operated in a nitrogen-free atmosphere to determine the importance of nitric acid in the corrosion mechanism. A 20-hour steady-state test was carried out using neat methanol as the fuel and a mixture of oxygen, argon, and carbon dioxide in place of air. The intake and

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20. ABSTRACT (Cont'd)

exhaust gases were frequently analyzed to be sure their compositions were constant and free of nitrogen. Emission measurements showed only trace amounts (1 ppm) of NO_x in the exhaust. Analysis of the condensates from the exhaust and blow also showed that only trace amounts of nitric acid were formed. The test showed that the wear indicated by iron buildup in the lubricant was essentially the same in the nitrogen-free test as that detected in baseline engine tests combusting methanol-air mixtures. It was concluded that nitric acid does not play a role in the corrosion of the upper cylinder bore and ring areas of methanol-fueled engines.

FOREWORD

The work reported herein was conducted at the U.S. Army Fuels and Lubricants Research Laboratory (AFLRL), Southwest Research Institute, San Antonio, TX, under Contract No. DAAK70-82-C-0001 and Department of Energy Interagency Agreement No. DE-AI01-79CS50030 and covers the period May 1983 - December 1983. The work was jointly funded by the U.S. Army Belvoir Research and Development Center, Ft. Belvoir, VA, and the U.S. Department of Energy, Heavy Duty Transport and Fuels Integration Branch. Contractor's representative was Mr. F.W. Schaekel, Materials, Fuels, and Lubricants Laboratory/STRBE-VF, and the technical monitor for the Department of Energy was Mr. G. Prok, NASA/Lewis, Cleveland, OH.

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I. INTRODUCTION

Several programs involving test engines (1-4)* and vehicle fleets (5) have shown that the use of neat methanol in spark ignition engines can cause unusually high levels of wear during conditions of warm-up and cold-weather operation. Test results from engines including a 350-CID V8, a 2.3-liter four-cylinder, and a single-cylinder CLR have shown that the increased wear principally occurs in the upper cylinder bore and ring areas. Surface profiles and electron micrographs of the cylinder bore and ring areas have indicated that corrosion plays a significant role in this wear mechanism.

Increases in wear were also observed in the exhaust valve guides, cam followers and lobes, and bearing surfaces, but these were much less severe than the cylinder bore and ring wear. It appeared that they arose from abrasive attack by metal oxide particulates which originated from the corrosion process in the cylinder bore.

Basically, three possible corrosion mechanisms have been proposed. Fuel impurities such as chlorine are known to cause corrosion in methanol-fueled engines.(6) It has been suggested (7) that nitric acid plays an important role in the corrosion mechanism since oxides of nitrogen are formed by combustion. Recent detection of combustion intermediates in the residues formed when methanol pools are allowed to burn to extinction indicate that formic acid and hydrogen peroxide cause the corrosion. The purpose of the present study was to determine the importance of nitric acid in the corrosion process.

II. BACKGROUND

Recently Ernst, et al. (7) compared the exhaust gas compositions of several test vehicles operating on neat methanol and gasoline. They found that

* Underscored numbers in parentheses refer to the list of references at the end of this report.

exhaust condensates from the methanol-fueled vehicles contained significantly higher concentrations of nitric acid than those vehicles fueled with unleaded gasoline. The pH of the exhaust condensates from the methanol-fueled vehicles reached levels as low as 1.75, while those from vehicles fueled with unleaded gasoline seldom fell below 2.5. Based on fleet test results, it was also found that the tendency toward wear was greatest in those methanol-fueled vehicles that produced the most acidic exhaust condensates.

Laboratory-scale engine testing at the U.S. Army Fuels and Lubricants Research Laboratory (AFLRL) showed that the wear rate was strongly dependent on the temperature of the oil and coolant.(2,4) Tests with both the 2.3-liter and the single-cylinder CLR engines showed that the wear rate increased dramatically as the temperatures of the oil and coolant were decreased.

The buildup of iron in the oil due to wear was highest at temperatures below the boiling point (65°C) of methanol; at temperatures above this level, the apparent wear rate became essentially equal to that for the same engine operating on unleaded gasoline. It was found that the buildup of iron in the oil at temperatures below 65°C was exponentially dependent on the temperature, that is, it had a dependence which could be expressed empirically as,

$$\ln(\text{iron conc.}) = b/T + c \qquad \text{(Eq. 1)}$$

where c is a constant and b is a temperature coefficient.

The wear rate observed at temperatures below 65°C was also found to depend on the engine load. At low load (<1500 RPM, 16 N-m), the wear rate measured with methanol in the 2.3-liter engine was about the same as that for unleaded gasoline. However, at a higher load (2500 RPM, 70 N-m), the wear rate for methanol greatly increased while that for unleaded gasoline was essentially unchanged.

Changes in the nature of the charge such as fuel prevaporization reduced the wear to about 60 percent of that observed in tests with a conventional carburetor. Although this was considered to be a substantial improvement, the actual wear was still significantly above the baseline level for unleaded gasoline.

The temperature dependence suggested that liquid fuel was present on the cylinder wall. If so, corrosive combustion products could diffuse to the surface and dissolve in the liquid layer. This seemed plausible because a simple model (8) for the evaporation of a liquid layer gave a reasonable prediction of the temperature dependence that was found for the wear rate. This model was based on the theory that as long as there was liquid fuel on the cylinder wall, deleterious combustion products could dissolve in the fuel, leaving a corrosive residue on the metal surface. It was assumed that the oil film was either diluted or washed off the upper cylinder wall by liquid methanol trapped in the crevice bound by the piston, ring, and cylinder wall. The model is based on Equation 2 which is basically Stefan's Law, taken from Spalding (8), for the rate of mass transfer through a stagnant film.

$$dm/dt = (D\ Rho/Fc)\ln(1+B) \qquad \text{(Eq. 2)}$$

m is the mass of the liquid evaporating, D is the coefficient of diffusion of methanol in the stagnant film, Rho is the density of methanol vapor calculated from the partial pressure at the liquid surface, Fc is the thickness of the stagnant film (essentially a boundary layer thickness), and B is the mass transfer number which is calculated from the partial pressure at the liquid and gas boundaries of the stagnant film. Although calculation of the absolute rate of evaporation of liquid from the cylinder wall was beyond the scope of this work, relative rates were adequate for predicting the temperature dependence. It is assumed in the model that the wear rate is proportional to the time required to evaporate fuel from the cylinder wall. Hence, the wear rate is inversely proportional to the evaporation rate, or

$$\text{wear rate} = k/(dm/dt) \qquad \text{(Eq. 3)}$$

where k is simply a proportionality constant. To compare theory with experiment, k was evaluated from a calculated evaporation rate and a measured wear rate at 52°C. Note, wear rate is an average value based on the iron buildup in a 20-hour test with a 2.3-liter, four-cylinder engine. Figure 1 shows that the model quite favorably predicts the observed effect of temperature on wear rate. Correlations of wear rate with temperature using Equation 1 showed that the temperature coefficient, b, of the theoretical wear rates (b = 10,490) was essentially the same as that based on observed wear rates (b = 10,400).

The effect of load on wear may also be elucidated by the theory t' . the formation of a liquid layer on the cylinder wall is a necessary step .. the corrosion mechanism. For sake of argument, assume that the fuel the combustion volume is totally vaporized. Since both manifold press\ and load increase correspondingly, the partial pressure of methanol in the combustion chamber at TDC must also increase. As the partial pressure of methanol increases, the dew point temperature increases. Calculations based on the manifold pressure and charge inlet temperature show that the dew points of methanol vapor at high load (2500 RPM, 96 N-m) and low load (1500 RPM, 16 N-m) are 135°F (57°C) and 107°F (42°C), respectively.

If the cylinder wall temperature as estimated from water jacket temperatures is not much above 50°C, condensation of methanol vapors on the cylinder wall is possible at high load but would not occur at the low load condition. It seems evident that any liquid fuel present on the cylinder wall would tend to evaporate prior to ignition at the low load condition; at high load, the fuel would stay on the wall until ignition and then burn off. During the burn off period, corrosive combustion products could dissolve in the liquid layer. This explains the fact that significant wear was also observed in tests where the methanol was totally vaporized before it entered the engine. It is cogent to assume that the liquid layer was formed on the cylinder wall by condensation of methanol vapors.

Exhaust gas samples were taken from the 2.3-liter engine at several conditions which included changing the temperature of the oil and coolant, as

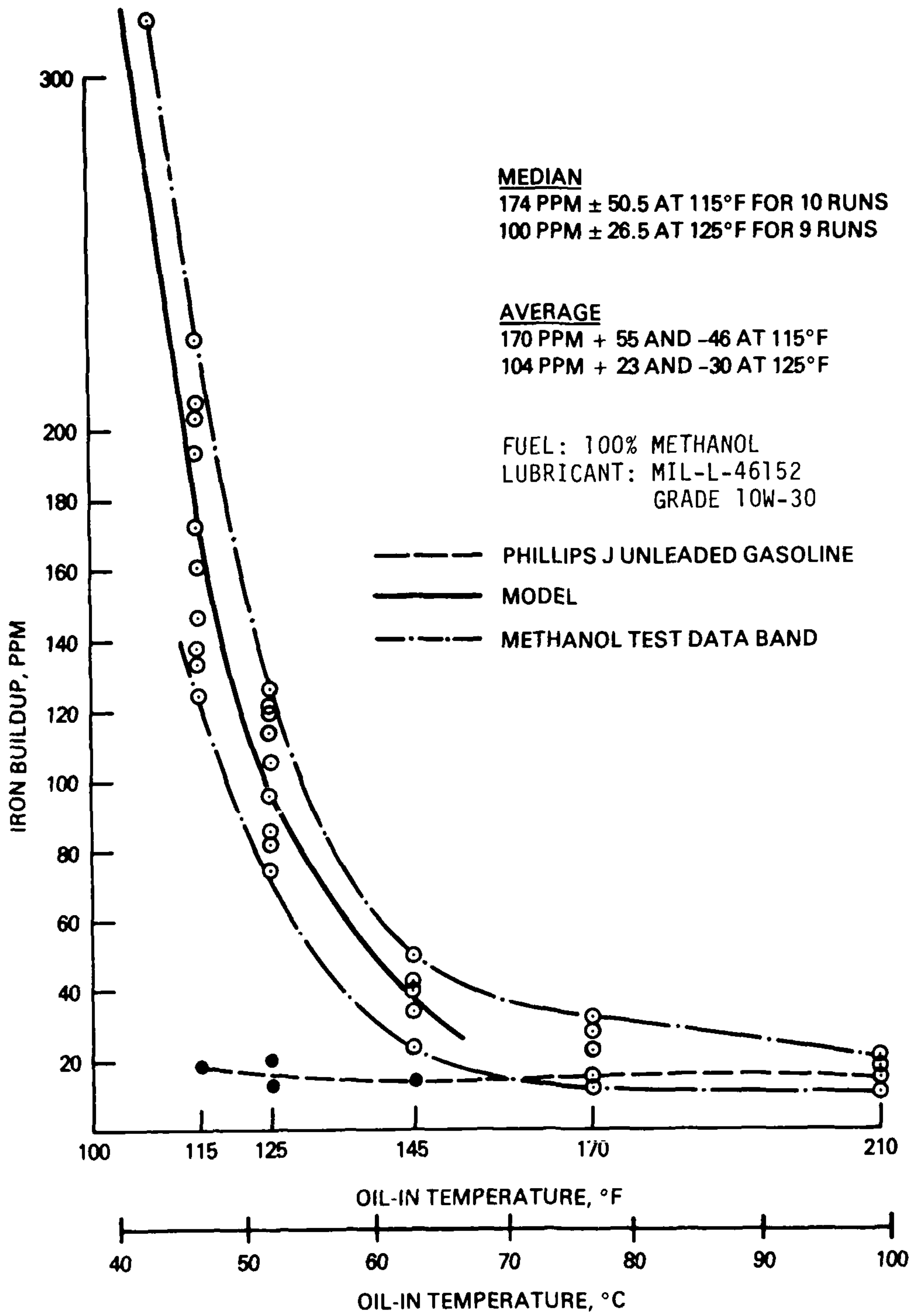


FIGURE 1. COMPARISON OF THE 2.3-LITER ENGINE 20-HOUR STEADY-STATE TEST DATA WITH THE SURFACE EVAPORATION MODEL

well as the load. The object was to determine the effects of fuel type and operating conditions on the formation of nitrogen oxides in the exhaust.

The results (9) in Table 1 show that methanol forms fewer total oxides of nitrogen in the exhaust than unleaded gasoline. Obviously, the total oxides of nitrogen increase sharply with increases in load and decrease when the temperatures of the oil and coolant are reduced. The subtle difference between methanol and unleaded gasoline is that the concentration of nitrogen dioxide in the exhaust is substantially higher for the former, and it increases quite dramatically as the oil and coolant temperatures decrease. In comparing different engine operating conditions in Table 1, it is clear that both nitrogen dioxide and the buildup of wear metals follow similar trends.

Since nitric acid is formed when nitrogen dioxide dissolves in water, one might conclude that it would be a favorable reactant in the corrosion process. It is important to note that the NO_x data presented in Table 1 are based upon the exhaust gas analysis and cannot be used to ascertain the presence of NO_2 in the combustion chamber. However, the possibility of NO_2 formation in the combustion chamber by the oxidation of unscavenged NO as well as prompt NO cannot be ruled out. If a liquid fuel layer is, in fact, present on the cylinder wall, it is conceivable that NO_2 and water formed by combustion could diffuse to the liquid and dissolve.

To determine the importance of nitric acid in the corrosion mechanism, a blowby diversion technique (10,11) was used to collect a sample of the condensate from the cylinder. The pH of the blowby condensate was in the range of 3.5 to 4, which was not close to the 1.8 reported by Ernst, et al. (7) for their exhaust condensate. The results indicated that very little nitric acid was formed in the combustion chamber. However, it was argued that the acid in the blowby may have been neutralized by metal surfaces in the sampling system or possibly alkali additives in the oil. It is important to note that the blowby condensate contained both oil and aqueous phases.

TABLE 1. IRON WEAR AND OXIDES OF NITROGEN

---Operating Conditions---

Description of Operating Condition	Torque (N-m)	Speed (RPM)	Oil Inlet (°C)	Coolant Out (°C)
Fast Idle, hot	16.3	1500	99	85
Fast Idle, cold	16.3	1500	51	46
Cruise, hot	94.9	2500	99	85
Cruise, cold	94.9	2500	51	46

---Measurements of Iron Wear and Oxides of Nitrogen---

Measurement	Fast Idle, Hot	Fast Idle, Cold	Cruise, Hot	Cruise, Cold
Methanol				
Iron wear, ppm	25	31	20	316
Total NO_x, ppm	31	22	2052	1937
NO, ppm	18	6	1645	1245
NO_2, ppm	13	16	407	692
Unleaded Gasoline				
Iron wear, ppm	25	30	20	17
Total NO_x, ppm	103	88.5	2690	2140
NO, ppm	100	85.5	2400	1905
NO_2, ppm	3	3	290	235

Source: AFLRL, Reference 8.

The possibility of measuring the concentrations of the oxides of nitrogen with a quick action gas-sampling valve designed to extract species from the cylinder wall boundary layer was considered, but temporarily ignored because of the ambiguities cited in the literature for such sampling techniques.(12,

13) The basic problem with that approach is that nitrogen dioxide can be formed by the oxidation of NO in the sampling line before an analysis can be made.

Recognizing the difficulties of detecting nitrogen dioxide and/or nitric acid in the combustion chamber, it was proposed that the least ambiguous aproach for determining the importance of nitric acid was to conduct a nitrogen-free engine test. By excluding nitrogen from the combustion gases, the high wear rate normally experienced with methanol would be significantly reduced if oxides of nitrogen are important.

III. APPROACH

The first problem in developing the experiment was the selection of a test engine that would provide measurable wear in a reasonable amount of time without consuming an inordinate amount of nitrogen-free oxidizer. It was also important that enough previous wear data were available on the engine so as to provide a good baseline for the nitrogen-free test. Both the Ford Pinto 2.3-liter four-cylinder and the single-cylinder CLR engines had sufficient test hours to satisfy the latter criteria, so the selection was based on the test duration and the amount of nitrogen-free gas required. The 2.3-liter engine was finally selected for the experiment because the duration of a test with this engine was 20 hours as opposed to 100 hours if the single-cylinder CLR engine was used. Based on test duration, engine volume, and RPM, it was also found that the 2.3-liter engine would consume the least amount of nitrogen-free gas.

The problem of providing a nitrogen-free atmosphere for a period of 20 hours had not been considered before and thus required some planning and consultation with gas suppliers. In previous studies, Herr, et al. (14) used a blend of 23 percent argon, 56 percent carbon dioxide, and 21 percent oxygen to replace air in a diesel engine; Spindt, et al. (15) used a blend of about 68 percent carbon dioxide and 32 percent oxygen in a spark ignition engine experiment. To compensate for the higher specific heat of carbon dioxide, Herr, et al. added argon and Spindt, et al. used a higher concentration of oxygen. For the present work, the argon/carbon dioxide/oxygen mixture was used because it provided a working fluid that was both thermodynamically and chemically similar to air. The above composition used by Herr, et al. provides the same specific heat ratio, gamma = 1.38, as air at room temperature. However, it is important to note that the gamma of that mixture will decrease relative to air at higher temperatures because the specific heat of carbon dioxide is more dependent on temperature than that of nitrogen. This reduces the adiabatic compression temperature, the adiabatic flame temperature, and the thermodynamic efficiency of the cycle. Since Herr, et al. did not report any difficulties in starting and maintaining load with their diesel engine, it was felt that the same mixture of oxygen, argon, and carbon dioxide would work adequately in the 2.3-liter spark ignition engine.

IV. TEST PROCEDURE

The gas supply system shown in Figure 2 was designed to deliver a blend consisting of 21 percent oxygen, 23 percent argon, and 56 percent carbon dioxide to the carburetor inlet of the 2.3-liter engine. The constituents of the nitrogen-free atmosphere were acquired from high-pressure gas cylinders using a combination of high-flow regulators to stepwise reduce pressure, and heaters to avoid regulator freeze-up. All the gases were handled in basically the same way, using one high-pressure regulator and one low-pressure regulator to reduce the pressure to about 5 psig. The lines before and after each regulator were wrapped with heating tapes, and in the case of carbon dioxide, a set of preheaters were placed in the line between the gas cylinders and the high-pressure regulator. The gases were passed through tube-in-core gas/liquid heat exchangers to adjust their temperatures to about 70°F (21°C). Flow rates were controlled by globe valves and measured with rotameters. The gases were then combined in a 114-liter mixing plenum, which contained fine and coarse mesh screens used to promote small- and large-scale turbulent mixing. The flow rates into the plenum were adjusted so that the pressure in the line leading to the carburetor inlet was in the range of 2 to 5 inches of water. Even though the system was sealed me-

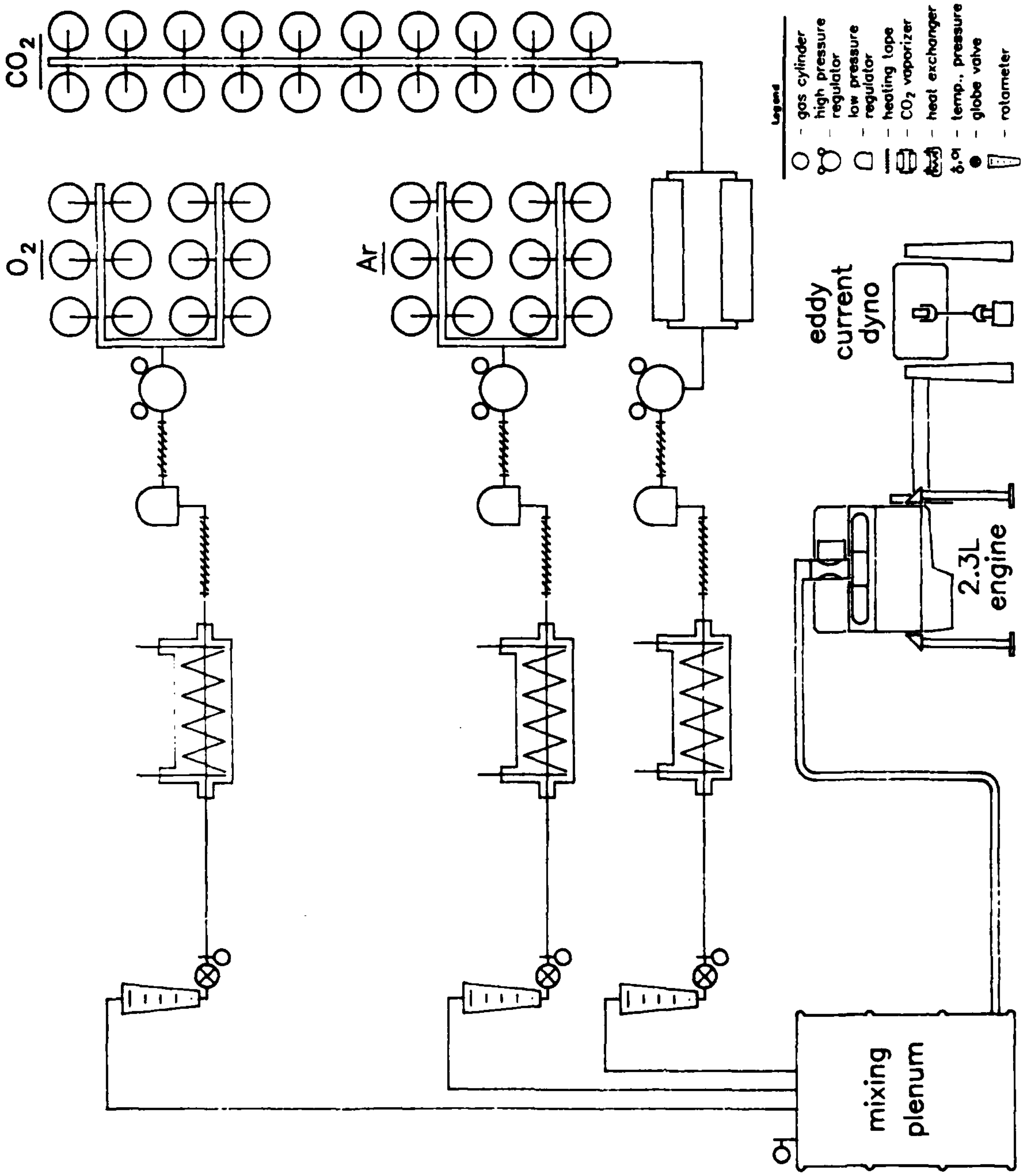


FIGURE 2. DIAGRAM OF NITROGEN-FREE GAS SUPPLY SYSTEM

ticulously, a positive line pressure was maintained wherever possible to prevent air contamination.

V. CHEMICAL ANALYSIS AND RESULTS

A. Gas Analysis

Gas chromatography was used periodically to monitor the concentrations of nitrogen, oxygen, argon, and carbon dioxide. The oxygen concentration was monitored continuously by a Beckman Monitor II analyzer. Regulated emissions of unburned hydrocarbons, carbon monoxide, and oxides of nitrogen were analyzed, respectively, by flame ionization (FID), nondispersive infrared (NDIR), and chemiluminescence.

Samples of the inlet and exhaust gases were collected in Tedlar® plastic bags and analyzed with a Varian model 1400 gas chromatograph equipped with a thermoconductivity detector. Exhaust gas samples were also analyzed for regulated emissions. A bellows pump was needed to pump the gases from the inlet and exhaust gas streams into the Tedlar® bags, because the pressure gradient between the stream and the bag was too low. Both the intake and exhaust gases were satisfactorily separated with a Porapak® Q, 80/100 mesh, column 10 feet in length and 1/8 inch in diameter using a helium carrier. A temperature program was devised to give discernible retention times of 2.02, 2.17, 2.30, and 7.51 minutes, respectively, for N_2, O_2, Ar, and CO_2. This analytical technique was particularly suitable because it allowed the detection of trace quantities of nitrogen in the midst of very high concentrations of argon, oxygen, and carbon dioxide. The detection limit for nitrogen was about 1000 ppm.

During the 20-hour engine test, the inlet and exhaust gas streams were analyzed periodically at about 100-minute intervals. The analyses were used to detect possible leaks in the system and ensure that flow rates were correct. Table 2 shows the mean values and the standard deviations of the inlet and exhaust gas compositions. Note the inlet gas compositions add up to

TABLE 2. INLET AND EXHAUST GAS COMPOSITIONS

Gas	Inlet Gases Mean	Inlet Gases Std Dev	Exhaust Gases Mean	Exhaust Gases Std Dev
Nitrogen (vol%)	0.18	0.10	0.37	0.12
Oxygen (vol%)	20.4	1.34	1.0*	----
Argon (vol%)	24.2	1.84	26.9**	2.65
Carbon Dioxide (vol%)	55.2	1.69	66.6	3.83
Carbon Monoxide (vol%)	----	----	2.0	----
Total Hydrocarbons (ppm)	----	----	500.6	----
Nitrogen Oxides (ppm)	----	----	1.0	----

* Oxygen concentrations measured with the Beckman Monitor II
** These values are the combined concentrations of argon and carbon monoxide. No correction was made for the difference in the TC detector response between argon and carbon monoxide

Source: AFLRL, 1983.

99.98 percent, while the total for the exhaust gases is 95.07 percent. The discrepancy in the exhaust gas composition is attributed to the fact that the analysis did not include combustion products such as water, formaldehyde, and unburned methanol. No attempt was made to measure the concentrations of these compounds, because they condensed in the Tedlar® bag.

B. Fuel

The fuel used in this study was commercial technical grade methanol meeting Federal Specification O-M-232d Grade A.

Although not well documented, it is well known (6) that trace amounts (>2 ppm) of chlorine can significantly accelerate engine wear in methanol-fueled engines. Tests at an automotive manufacturing company indicate that accelerated wear is not discernible until the chlorine content of the fuel exceeds 2 ppm. The methanol used in this work was analyzed for total chloride, i.e., both inorganic and organic forms. The total chloride content determined by coulometry was 0.6 ppm. A second analysis using ion chromatography showed that the inorganic portion of the total chloride was 0.3 ppm. This chloride contamination is well below the deleterious level and would not affect the results of the nitrogen-free engine test.

C. Exhaust Gas and Blowby Condensates

A portion of the exhaust was passed through an ice-cooled trap for approximately 14 hours of the test period. About 100 mL of an aqueous condensate was recovered from the trap. The blowby gases issuing from a port in the crankcase of the engine passed through a similar trap for the full duration of the test. The blowby condensate consisted of a highly viscous milky emulsion of oil, water, and combustion products. Centrifuging would not break the emulsion into its oil and aqueous phases, but upon standing, small globules of the aqueous phase separated. This allowed the extraction of a small amount of the aqueous component. Table 3 gives a summary of the analysis of the aqueous blowby component and the exhaust gas condensate.

TABLE 3. BLOWBY AND EXHAUST CONDENSATE COMPOSITIONS

Analysis	Exhaust Condensate	Blowby Condensate
Formaldehyde (ppm)	1523.0	1650.0
Formate ion (ppm)	56.0	ND
Nitrate ion (ppm)	100.0	ND
Chloride ion (ppm)	2	--
Sulfate ion (ppm)	300	--
pH	3.9	8.5
Water (wt%)	--	61.0
Methanol (wt%)	--	18.4
Oil (Wt%)	--	20.4

ND - No detection

Source: AFLRL, 1983.

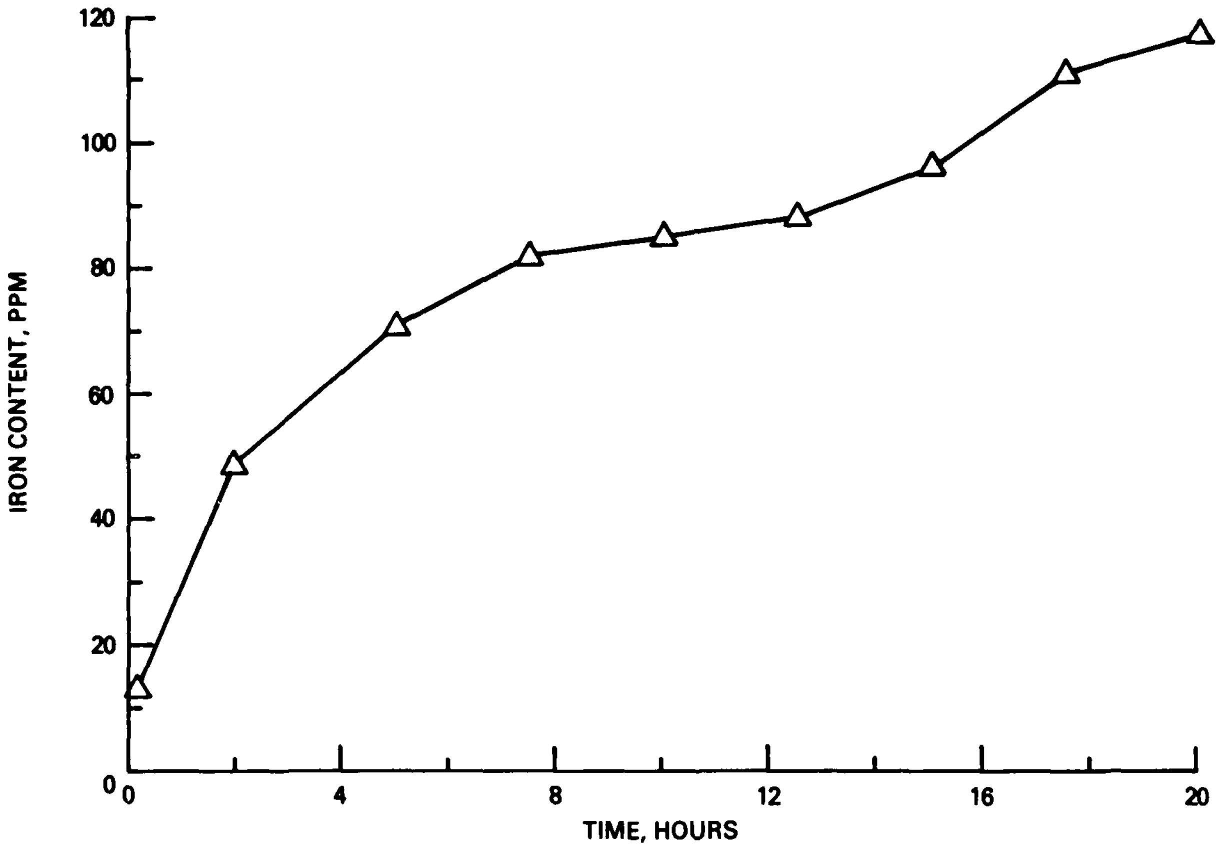
The pH measurements were made with a L&N model 7415 pH meter equipped with a micro dual-electrode sensor. Formaldehyde was analyzed by a colorimetric method (16), and formate, nitrate, chloride and sulfate ions were determined by ion chromatography. In addition to these anions, X-ray fluorescence showed that the condensate contained traces (<25 ppm) of iron, calcium, and zinc.

D. Wear Metals in Oil

Several oil samples were withdrawn from the engine for wear metals analysis by X-ray fluorescence.(17) It was found in previous test programs that the buildup of iron in the oil was the most sensitive and accurate method of gauging the engine wear. Figure 3 shows the buildup of iron in the oil for the 20-hour nitrogen-free engine test. In addition to iron, the analysis also included copper, chromium, lead, and aluminum. However, the concentrations of these metals were found to be below the minimum detection limits which were 10, 15, 60, and 250 ppm, respectively, for copper, chromium, lead, and aluminum. In Figure 4, the total buildup of iron (117 ppm) in the nitrogen-free test is compared with the results of several other engine tests in which air was used as the working fluid. It is clear that the iron content of the oil in the nitrogen-free test falls well within the error band of previous tests.

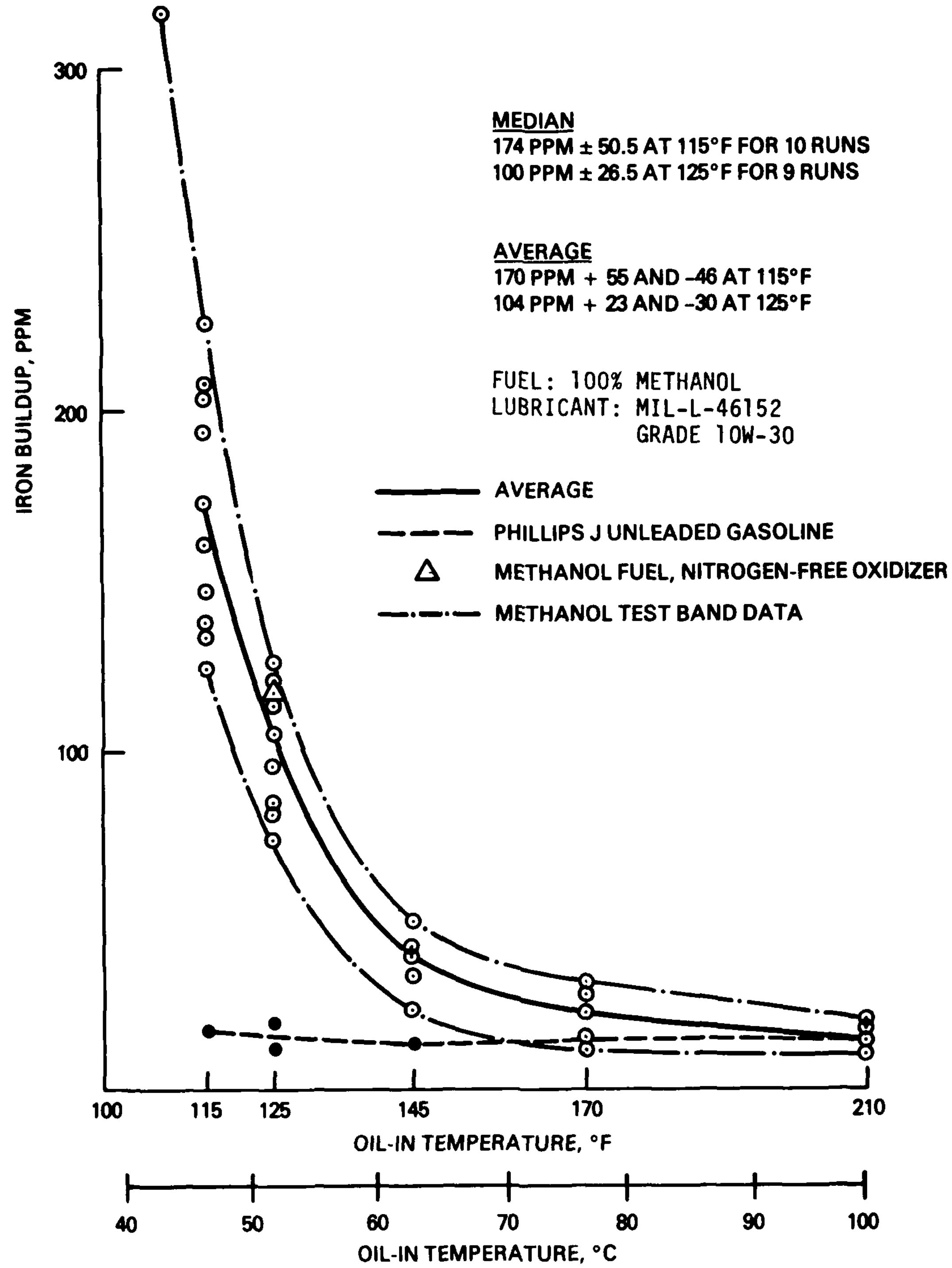
E. Lubricant Analysis

The oil analysis consisted of viscosity, total acid number (TAN), total base number (TBN), and water content. The viscosity was measured before and after the test by the D 445 ASTM Method. TAN and TBN were determined by D 664 ASTM Method, and the water content was measured by titration with Karl Fischer reagent. The test results are compared in Table 4 with typical lubricant analyses of the same oil used in previous engine tests using neat methanol as the fuel and air as the working fluid.



Source: AFLRL, 1983.

FIGURE 3. HISTORY OF IRON BUILDUP IN THE OIL FOR THE NITROGEN-FREE ENGINE TEST WITH METHANOL



Source: AFLRL, 1983.

FIGURE 4. 2.3-LITER ENGINE 20-HOUR STEADY-STATE TESTS

TABLE 4. LUBRICANT ANALYSIS

Determination	Nitrogen-Free Test	Baseline Test*
Viscosity, cSt @ 40°C, (N)	68.9	68.9
Viscosity, cSt @ 40°C, (U)	50.7	58.5
Total Acid Number (N)	2.3	2.3
Total Acid Number (U)	2.3	2.4
Total Base Number (N)	9.7	9.7
Total Base Number (U)	5.4	5.5
Water Content, wt% (U)	0.5	0.4
Methanol Content, wt% (U)	0.1	---

(N) - New oil, (U) - Used oil

*Source: Reference 4.

VI. DISCUSSION OF RESULTS

The results of the nitrogen-free engine test were remarkably similar to those obtained in previous tests (1-4) in which air was used as the working fluid. The first and most significant result of the experiment was that the iron buildup in the lubricant was essentially the same as that measured in baseline tests. This observation alone precluded the importance of nitrogen oxides in the corrosion mechanism.

Throughout the engine test, the engine performed favorably. As compared with the baseline tests, the engine load was approximately 15 percent low and the fuel consumption was approximately 5 percent higher than normal. No attempt was made to increase the load because that would have required an increase in the flow of nitrogen-free oxidizer. This observed reduction in thermodynamic efficiency was expected because the average specific heat ratio for the nitrogen-free working fluid was lower than that of air.

Slightly higher temperatures found in the exhaust gas and the coolant leaving the engine also gave an indication that the thermodynamic efficiency was reduced. The emissions measurements showed that the concentrations of oxygen (ca. 1 percent), carbon monoxide (ca. 2 percent) and unburned fuel (ca. 500 ppm) in the exhaust were the same as those measured in baseline tests with air.(9) This was a good indication that the combustion efficiency in the nitrogen-free test was the same as that observed in the baseline test.

Periodic analysis of the inlet and exhaust gases showed that composition was reasonably constant throughout the 20-hour test and that contamination due to air leaks in the system was negligible. The nitrogen in the exhaust gas was slightly higher (about 3500 ppm) than that of the inlet gas (1000 ppm), indicating that some leakage occurred. This air entrainment most probably occurred at the seals between the cylinder head, manifold, and carburetor. Shortly after the test conditions were stabilized, the throttle shaft was sealed with a flexible silicone rubber resin, and a shroud purged with carbon dioxide was placed around the carburetor. The small nitrogen leak was of little consequence because emissions analysis showed only trace amounts of NO_x (about 1 ppm).

The exhaust condensate had a pH of 3.9 and contained about 100 ppm nitrate ion, 56 ppm formate ion, 2 ppm chloride ion, and 300 ppm sulfate. A pH of 3.9 can be achieved by dissolving only 5 ppm of formic acid in water. The actual concentrations of anions detected in the condensate indicate a much lower pH. It appears that the observed pH is due to the presence of cations (iron, calcium, and zinc) in the condensate.

The iron is expected in the condensate because it is a product of the cylinder bore and ring wear. Calcium, zinc, and sulfur are released in the combustion of additives in the lubricant. The formate and chloride ions are derived from the combustion of the fuel. Nitrate appears to be formed from the oxidation of traces of nitrogen in the system as well as organically bound nitrogen in the lubricant. It is not surprising that some nitric acid was found since the accumulation time for the condensate sample was 14 hours. Condensate samples obtained by Ernst, et al. (7) were generated in less than an hour using air as the working fluid and had acid concentrations that were more than a hundred times greater than that observed in the nitrogen-free experiment.

The blowby condensate was a highly viscous emulsion of an aqueous phase and the lubricant. Upon standing, small globules of the aqueous phase separated from the emulsion. Otherwise, the emulsion appeared to be very stable because extended centrifuging would not cause any further separation of the phases. Analysis of the aqueous globules showed that they were alkaline with a pH of about 8.5 and did not contain any formate or nitrate ions. If acids were originally present, it appears that they were neutralized and absorbed by alkaline additives in the lubricant portion of the blowby.

Analyses showed that the lubricant underwent chemical and physical changes in the nitrogen-free test which were basically equivalent to those found in baseline tests with the same oil. The strong similarity in the total acid and base numbers between the nitrogen-free and baseline tests suggests that the lubricant in the baseline tests was not significantly contaminated with nitric acid. It seems safe to conclude that organic acids contribute mainly to the depletion of alkaline additives in the oil. Ernst, et al. (7) measured relatively low values of pH (>2) in blowby condensates and concluded that significant concentrations of nitric acid are formed in the engine crankcase. The results of the present study indicate that very little nitric acid, if any, is scavenged by the lubricant in the crankcase. Instead, it seems that the oxides of nitrogen, NO, and NO_2 remain in the gas phase while they are present in the engine. When a condensate sample is obtained, the gases are essentially purged through an aqueous medium. This intimate contact between NO_2 and water is the primary process for creating nitric acid (18).

Marteney (19) did kinetic modeling of the nitrogen oxide formation in hydrocarbon-air combustion. The results of these calculations showed that nitric oxide formation is very slow and occurs, for the most part, after hydrocarbon oxidation is complete. The reason for this is twofold: 1) the rate-controlling step in the Zeldovich mechanism, i.e., $O + N_2 = NO + O$, is relatively slow when compared with hydrocarbon oxidation reactions, and 2) this reaction has a very high activation energy and requires high concentrations of O atoms so the rate does not become appreciable until the temperature is high (> 2000K). At high combustion temperatures, NO_2 is thermodynamically unstable and equilibrium calculations (19) show that its concentration would be about 10^{-4}x[NO] in the combustion product gases. Based on measurements of exhaust gas emissions from the 2.3-liter engine operating on a methanol-air mixture, the concentrations of NO and NO_2 in the combustion chamber would be about 2000 ppm and 0.2 ppm respectively. The only other source of NO_2 in the combustion chamber is the oxidation of unscavenged NO. Considering that NO is reduced significantly by dilution and that the unscavenged exhaust gases have a much lower density than the incoming cool methanol-air charge, the concentration of NO in the new fuel/ air mixture would be about 100 ppm. The oxidation of NO to NO_2 in air is a termolecular reaction (20), i.e., $2NO + O_2 = 2NO_2$, which is too slow to account for a significant buildup of NO_2 in the duration of the intake and compression strokes. Calculations of the rate of this reaction using the rate constant given in Benson (20) show that the half life of NO (50 percent conversion to NO_2) would be about 2 hours.

Anderson, et al. (21) kinetically modeled the combustion reactions in the combustion chamber and exhaust of a turbojet. The model predicted that NO_2 did not form in the combustion chamber, but was formed later in the relatively cool exhaust after the nozzle expansion. They concluded that NO was oxidized to NO_2 by HO_2 radicals formed by the oxidation of hydrocarbons present in the exhaust. It is quite evident from these modeling efforts and calculations given above that only trace amounts of NO_2 could be present in the combustion volume of a spark ignition engine.

These kinetic arguments tend to rule out the presence of nitric acid in the combustion chamber, and they are consistent with the fact that the buildup of iron in the oil in the nitrogen-free test fell well within the error band of the baseline test data shown in Figure 4. It is most improbable that this coincidence is an anomalous result; the experimental results give all indications that the test was normal and predictable, and chemical analyses showed conclusively that the oxides of nitrogen were only present in trace amounts. The evidence overwhelmingly supports the conclusion that nitric acid does not play a role in the corrosion mechanism.

In parallel with the work reported here, a fundamental research program has been in progress to investigate possible corrosion mechanisms that involve intermediate products formed in the combustion of methanol.(22) This work is based mainly on the combustion of methanol pools and burning liquid layers. Experiments were carried out in shallow metal dishes about 5 cm in diameter and 6 mm in depth. The three dishes used in the experiments were made of cast iron, aluminum, and stainless steel. When a dish was filled with methanol and allowed to burn until the flame self extinguished, a liquid residue remained. The residue volume decreased sharply as the molecular weight of the alcohol burned was increased. Hydrocarbons such as isooctane did not leave a residue. Residues formed from methanol in the aluminum and stainless steel dishes were aqueous solutions containing about 25 percent methanol, 1.5 percent formaldehyde, 2000 ppm formic acid, and 1000 ppm hydrogen peroxide. When methanol was burned in the cast iron dish, the residue still contained about 25 percent methanol and 1.5 percent formaldehyde, but the formic acid and hydrogen peroxide were not present. Further analysis showed that this residue contained about 1000 ppm of iron and 2000 ppm of formate ion. These results showed that the formic acid and hydrogen peroxide attacked the iron surface, forming an iron formate salt.

It is well-known that hydrogen peroxide is an intermediate in the combustion of all alcohol and hydrocarbon fuels.(23) There is some evidence for the formation of formic acid in the combustion of alcohols, namely methanol (24), which yields higher intermediate concentrations of formaldehyde; kinetic studies (25) tend not to rule out the formation of formic acid. In burning methanol pools, the combustion intermediates including water, formaldehyde, formic acid, and hydrogen peroxide diffuse to the liquid surface and dissolve. Residues are not formed in burning hydrocarbon pools because the combustion intermediates are not soluble. This is basically the reason why this corrosion mechanism is not important in the combustion of nonpolar fuels such as gasoline.

VII. CONCLUSIONS

A nitrogen-free engine test was performed to determine the importance of nitric acid in the corrosion of the upper cylinder bore and ring areas of methanol-fueled engines. The test results gave all indications that the engine performance and combustion efficiency were similar to those observed in baseline tests with air. Analysis of exhaust emissions, exhaust condensate, and blowby condensate showed that only trace amounts of nitrogen oxides were present in the engine. Wear measured in terms of iron buildup in the lubricant was found to be essentially the same in the nitrogen-free test as that detected in baseline engine tests combusting methanol-air mixtures. This work shows conclusively that nitric acid does not play a role in the corrosion of the upper cylinder bore and ring areas of a methanol-fueled engine. A basic study of the combustion intermediates found in the residue of burned pools of methanol suggests an alternative mechanism in which iron corrosion is caused by formic acid and hydrogen peroxide.

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